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Synthesis and characterization of tetraethylammonium tetrachloro cadmiate crystals

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Abstract Single crystals of tetraethylammonium tetrachloro cadmiate, abbreviated as TEATC-Cd, were grown by slow evaporation method in saturated aqueous solution at room temperature (28°C). The crystals obtained were bright, transparent and colourless having a size of about $8 \times 6 \times 2$ mm^3. The grown crystals were characterized through elemental analysis, powder XRD, thermogravimetric analysis (TGA), differential scanning calorimetric analysis (DSC), Fourier Transform Infrared (FTIR) and NMR spectroscopic techniques. The elemental analysis confirms the stoichiometry of the synthesised compound and the powder XRD pattern ensures its crystallinity. The TGA thermogram indicates weight losses at 410.2°C and 684.1°C from which the decomposition pattern is formulated. The DSC study shows thermal variations at temperatures 8°C, 123.5°C and – 146.4°C during the cooling cycle and at temperatures 1.5°C, – 14.1°C, – 122.2°C and – 161°C during the heating cycle which shows first and second order phase transitions. The IR spectroscopic data were used to assign the characteristic vibrational frequencies of tetraethyl ammonium (TEA^+) ions and $CdCl_4^{2-}$ ions. The NMR spectrum confirms the presence of two kinds of protons in the ethyl group of the compound.

Keywords Solution growth, tetraethylammonium tetrachloro cadmiate crystals, phase transition, characterization

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1. Introduction

Tetraethylammonium tetrachloro cadmiate, abbreviated as TEATC-Cd, belongs to the family of crystals A_2BX_4 where A = univalent cation, NH_4^+, $N(CH_3)_4^+$ and $N(C_2H_5)_4^+$, B = divalent cation like Cu^{2+}, Co^{2+}, Ni^{2+} and X = Cl, Br and I. Most of the crystals in this family show incommensurate-commensurate phase transitions and ferroelectric behaviour in a narrow temperature range in the commensurate phase [1-3]. Stucky *et al* [4] determined the crystal structure of tetraethylammonium compounds (TEATC-Ni and TEATC-Co). The space groups of these crystals were found to be P42/*nmc* with $n = 2$. Most of the crystals in this family are isomorphous. Compounds of this type containing ethyl groups show at most only two phase transitions at low temperatures. Kahrizi and Stmitz[5] have carried out structural phase transition in $(TEA)_2CdX_4$ compounds through thermal expansion measurements. Iwata and Ishibashi [6] studied dielectric dispersion in $(TEA)_2ZnCl_4$ crystals. In these type of crystals, large thermal hysteresis was found which indicates that these crystals are associated with first order phase transition.

The present paper deals with the preliminary studies of synthesis and characterization of TEATC-Cd crystals through elemental analysis, powder XRD, TG-DTG and DTA studies, DSC, FTIR and NMR spectra.

2. Experimental

Single crystals of TEATC-Cd were obtained by mixing aqueous solutions of tetraethyl ammonium chloride (E Merck, Germany) and $CdCl_2.H_2O$ (GR grade) chemicals in 2:1 stoichiometric ratio. The solutions were thoroughly mixed, filtered and allowed to evaporate slowly at about 28°C with minimum mechanical disturbance. Single crystals of the compound were obtained in about 12-14 days time. The crystals obtained were (Figure 1) bright, transparent and colourless with an average size of $8 \times 6 \times 2$ mm^3. The crystals are soluble in water, but dissolve only

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sparingly in ethanol. The melting point of the compound was recorded as 286°C. The elemental analysis (C, H and N) of the compound was carried out using Heraeus Carlo Erba 1108 instrument to verify its stoichiometry. A JEOL (Japan) JDX 8030 XRD instrument with CuKα radiation of λ = 1.5418Å was used for obtaining the X-ray powder diffraction pattern. The TG and DTA analyses were done using NETZSCH-Geratebau GmbH thermal analyser in nitrogen atmosphere with a heating rate of 10 K min^{-1}. The DSC analysis was undertaken using NETZSCH DSC analyser under nitrogen atmosphere at a heating rate of 10 K min^{-1}. The FTIR and far IR spectra of the crystals were obtained by means of Bruker IFS66V Spectrometer using KBr pellet technique between 4000-100 cm^{-1} region. The NMR spectrum of the crystals was obtained using Bruker DPX instrument.

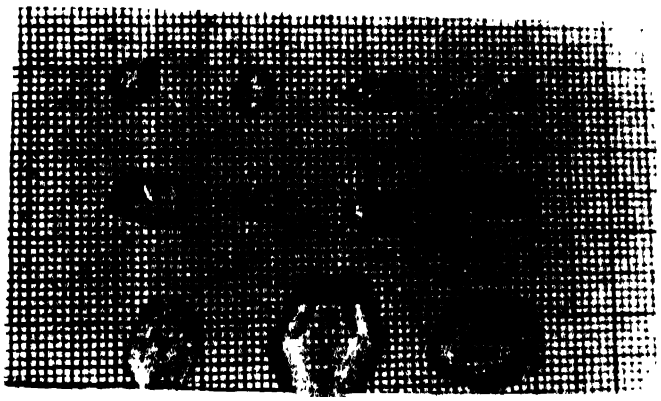


Figure 1. Photograph of the grown crystals of TEATC-Cd

3. Results and discussion

The elemental (C, H and N) analysis given in Table 1 confirms the stoichiometry and hence the formula of the synthesised crystals. The difference between calculated and observed percentage elemental compositions is found to be very small and within experimental errors. The X-ray diffraction powder pattern of the grown crystals is shown in Figure 2. The sharp and well defined peaks confirm the crystallinity of the compound.

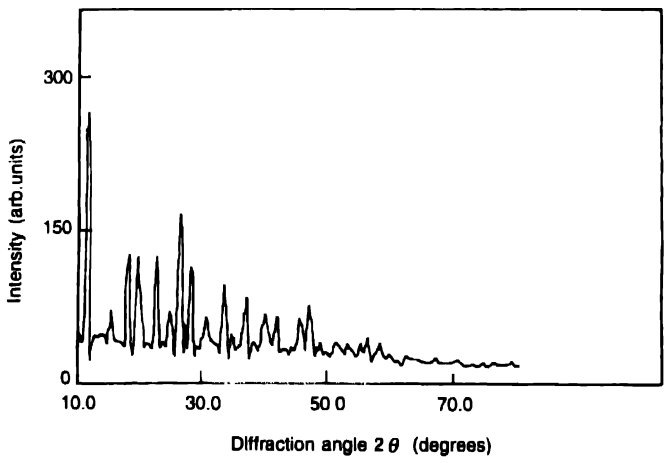


Figure 2. X-ray powder diffraction pattern of TEATC-Cd

Table 1. Elemental analysis (C, H and N).

	C%	H%	N%
Calculated	37.35	7.78	5.44
Experimental	37.54	8.24	5.01

The TG and DTA thermograms are shown in Figures 3 and 4 respectively. The following decomposition pattern is formulated.

Step I

$$[N(C_2H_5)_4]CdCl_4 \xrightarrow{311.2^{\circ}C} N_2\uparrow + 4C_4H_{10}\uparrow + CdC$$

TEATC-Cd

Formula weight 514.2 $\quad 28 + 4\times58$ (260) $\quad$ 254

Step II

$$CdCl_4 \xrightarrow{410.2^{\circ}C} CdCl_2 + Cl_2$$

254 $\quad$ 183.2 $\quad$ 71

Step III

$$CdCl_2 \xrightarrow{684.1^{\circ}C} Cd\uparrow + Cl_2\uparrow$$

183.2 $\quad$ 112.2 $\quad$ 71

(183.2)

The decompositions of the compound at 311.2°C (step I) and at 684.1°C (step III) fit well with the observed weight losses at these temperatures. A slight higher weight loss (4.4 %) at 410.2°C in step II compared to the observed weight loss may be due to simultaneous occurrence of steps II and III. As observed in Figure 3, the step II decomposition process takes place only within a short temperature range.

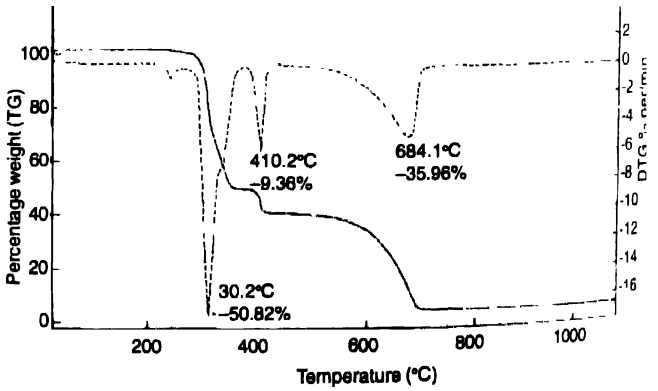


Figure 3. TG and DTG thermograms of TEATC-Cd.

In the DTA curve (Figure 4) the endothermal dip at 289.4°C corresponds to the melting point (286°C) of the compound. The decomposition of the compound starting at 311.2°C (Figure 3) is evident from the hump in DTA curve at 312.9°C. The deep endothermal dip in DTA curve at 502 4°C may be due to the higher energy requirement for the decomposition of $CdCl_2$ in step III

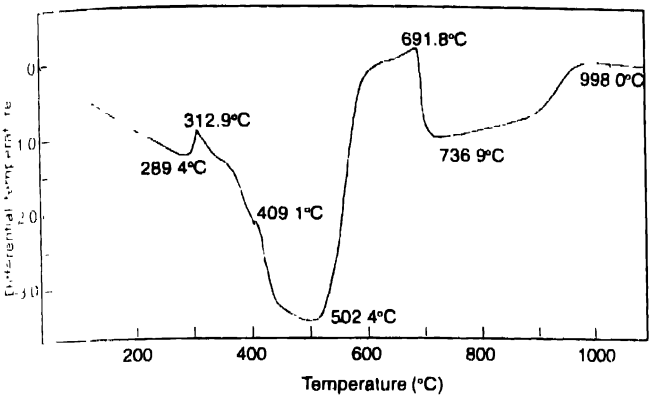
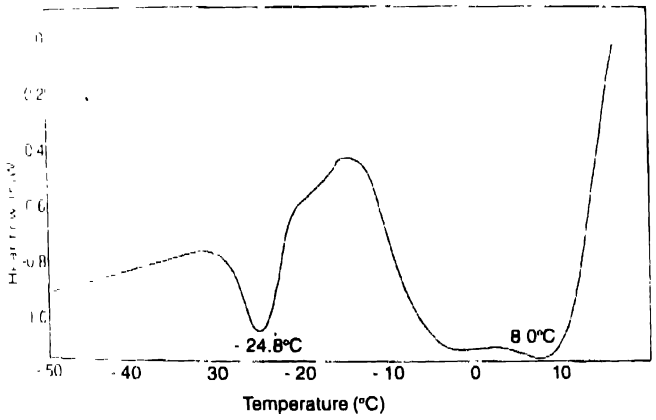
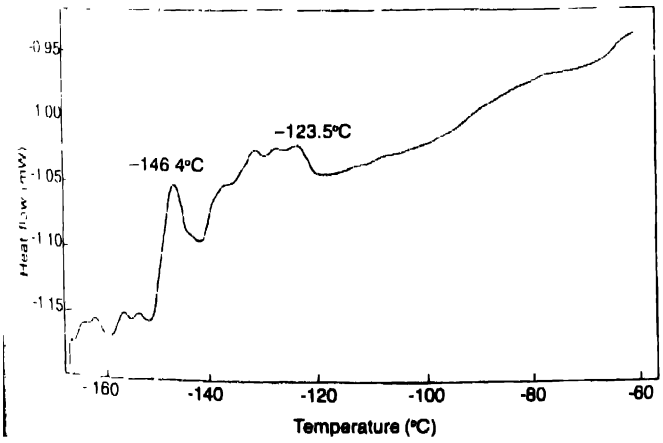


Figure 4. DTA thermogram of TEATC-Cd

The DSC curves (Figure 5) show thermal anomalies at 8°C, 21.8°C, -123.5°C, and -146.4°C in the cooling cycle and at 1.5°C, -14.1°C, -122.2°C and -161°C in the heating cycle. This suggests that the crystal undergoes mostly first order phase transitions as observed in the corresponding thermal hystereses at temperatures 8°C, -24.8°C, -146.4°C and 1.5°C, -14.1°C, -161°C





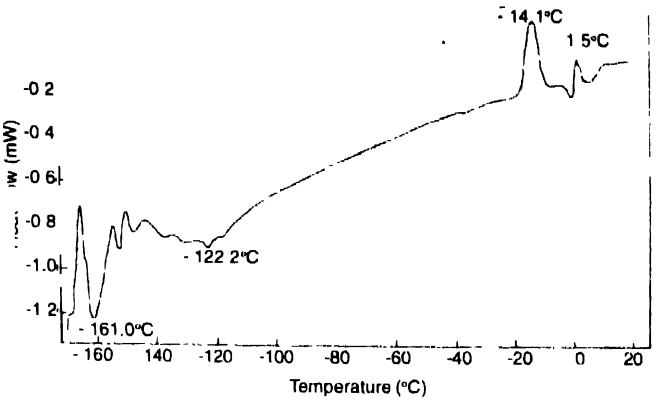


Figure 5. DSC curves of TEATC-Cd

during the cooling and heating cycles respectively. The thermal anomaly at -123.5°C in the cooling cycle and at -122.2°C in the

Table 2. IR and far IR spectral data of TEATC-Cd

Wave number cm^{-1}	Assignment
3598.7	Asymmetric C-H stretching vibration in TEA group
2987 7 2947 6	Symmetric C-H stretching vibrations in TEA group
1487 3	Asymmetric deformation in CH_3 group
1455 6	δ Asymmetric CH_2
1392 9	δ Symmetric CH_3
1366 3	δ Asymmetric CH_3
1305 6	CH_2 twist
1184 1	CH_3 rocking
1079 6	γ Asymmetric C-C
1033 6	γ Asymmetric C-N
1004 7	CH_3 rocking
897 3 (weak band)	γ Symmetric C-C
787 6	CH_2 rocking
468 3	δ C-C-N
409 6	Librational modes of substituted ammonium ion in TEA group
481 3 470 6 455.9 422.3	Skeletal TEA vibrations
256 3 236 2 107.8	$CdCl_4^{2-}$ internal vibrations

heating cycle is very close suggesting second order type of phase transition.

The FTIR and far IR spectra (Figure 6) were used to identify the compound. The various characteristic absorption bands and their assignments are summarised in Table 2. From the spectra it is observed that the crystals do not contain water molecules in any form. The absorption bands at 3598 cm^{-1} is due to C–H asymmetric stretching and bands at 2987-2947 cm^{-1} are due to C–H symmetric stretching vibrations in TEA group. The δ asymmetric and δ symmetric CH_3 absorptions are found at 1455 and 1392 cm^{-1} respectively. The CH_2 twisting mode of vibration is observed at 1305 cm^{-1}. The absorption band at 1184 cm^{-1} is due to CH_3 rocking. The C–C asymmetric and C–N asymmetric absorption frequencies are observed at 1079 and 1033 cm^{-1} respectively. The absorption band at 1004 cm^{-1} represents another rocking vibrational mode of CH_3 in C_2H_5 group present in TEATC–Cd. The symmetric C–C vibration observed at 897 cm^{-1} is found to be weak in intensity. The peak at 787 cm^{-1} represents CH_2 rocking mode. The absorption at 468 cm^{-1} is assigned to C–C–N vibration. The absorptions at 481, 470, 455 and 422 cm^{-1} are due to TEA skeletal vibrations. The $CdCl_4^{2-}$ internal vibrations are found to occur at 256, 236 and 107 cm^{-1}. The assignments of the various absorption frequencies for the crystals are found in good agreement with those of similar compounds [7-9].

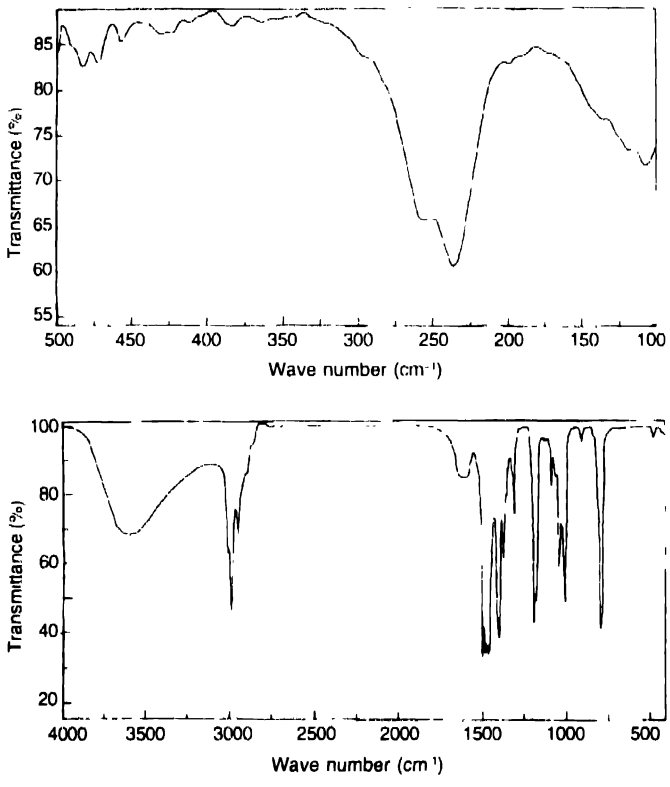


Figure 6. Infrared spectra (FTIR and far IR) of TEATC-Cd

The NMR spectrum shown in Figure 7 confirms the presence of only two kinds of protons in the ethyl group of the compound as expected. The methylene protons (CH_2) and methyl protons (CH_3) appear at 1 ppm and 3 ppm respectively.

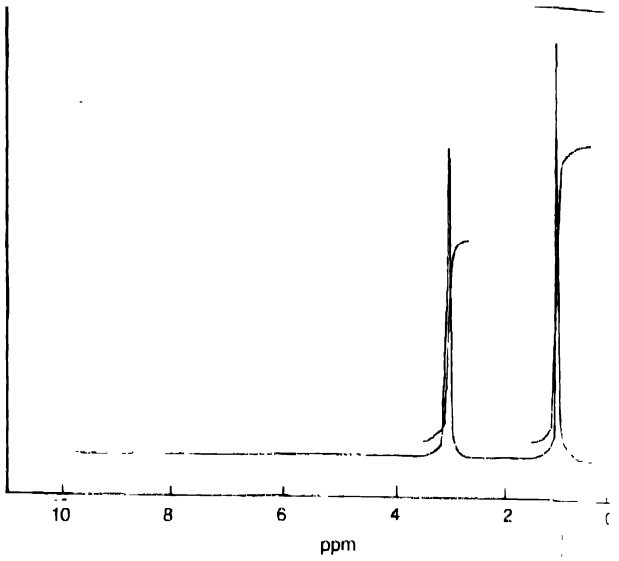


Figure 7. NMR spectrum of TEATC-Cd

4. Conclusions

Single crystals of TEATC-Cd were obtained by employing slow evaporation solution technique. The grown crystals were bright transparent and colourless. The C, H and N elemental analysis of the compound confirms its stoichiometry. The X-ray powder diffraction pattern with sharp and well defined peaks at specific (2θ) angles indicate the crystallinity of the synthesised compound. The TGA studies are used to formulate the decomposition pattern of the compound. The DSC study indicates that the crystal undergoes mostly first order phase transition. The FTIR and far IR spectra of the crystal show clearly the characteristic absorption frequencies of both TEA^+ and $CdCl_4^{2-}$ tetrahedra present in the compound. The NMR spectrum confirms the presence of both methylene and methyl protons of the ethyl group present in the crystalline crystalline compound. Raman spectroscopic studies of structural phase transitions for the grown crystals are in progress.

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